

D E C L A R A T I O N

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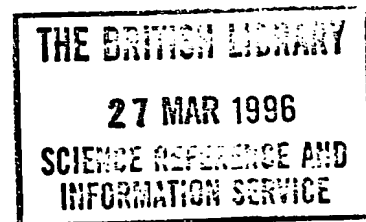
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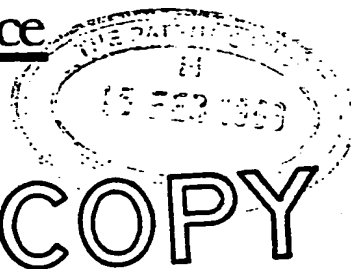
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The interest in the properties of materials in the nano-scale range has recently increased enormously. With various metals it has been shown that many physical properties of compact materials in the nano-scale range are tremendously different from those of corresponding more coarse and crystalline products (e.g. density, specific heat, chemical properties). This is attributed to the high proportion of interface atoms which are not in the "normal" state of the atoms of the "inner" crystal lattice. While the metals are already studied quite well, the state of the research with the oxides is still significantly less developed. However, theoretical considerations and initial experimental findings on  $\text{TiO}_2$  show that nanocrystalline materials having crystallite sizes ranging from 1 to 10 nm show a plastic behaviour comparable to metallic materials already at low temperatures.

Through other studies on ceramic materials in the nano-scale range significantly lower sintering temperatures have been determined in comparison to conventional sub- $\mu\text{m}$ -powders. Thus, it was for example shown that  $\text{ZrO}_2$  powders having crystallite sizes around 5 nm sinter already at  $1100^\circ\text{C}$  to afford 94% of the theoretical density. In comparison to presently available sub- $\mu\text{m}$ -powders this means a reduction of the sintering temperature by more than  $500^\circ\text{C}$ .

In addition to basic physical phenomena relating to materials interesting aspects with respect to properties relating to materials of ceramic materials prepared from nanocrystalline oxides are also provided. Apart from the mentioned process aspects (low sintering temperatures), problems regarding the ductility and the homogeneity of the structures are of particular interest. If one succeeded in stabilizing such structures also at higher temperatures and if the hints obtained from previous studies could be confirmed, ceramics having interesting new properties should be available via nanocrystalline structures.

In view of said background, ceramic powders in the nano-scale range are of increasing interest as starting materials and various processes for their preparation have been described in the

literature. Apart from various gas phase processes said processes have recently also included chemical syntheses from solution such as the sol-gel process, the hydrothermal synthesis and the emulsion technique.

In said processes particles are generated by growth processes (in most cases condensation reactions from molecular precursors such as dissolved salts, hydroxides or alkoxides). The control of the size of said particles and avoiding the "growing together" of such particles are critical since said particles have highly reactive surfaces due to their generation process.

The sol-gel process is a synthesis method wherein first a sol, i.e., soluble polycondensates having oligomeric or polymeric structure, or colloidal solutions are prepared by hydrolysis and condensation reactions of suitable starting compounds (salts, metal alcoholates) in a solvent. The proceeding reaction then results in the formation of a solid body, the gel, which subsequently is converted into a crystalline ceramic powder by a thermal post-treatment. However, by suitably controlling the reacting conditions it is also possible to "freeze" said process at the stage of the sol and to generate in this manner particles having average diameters ranging from 1 to 50 nm. However, the high proportion of OH groups on the surfaces of the particles renders an agglomerate-free isolation and calcination of powders in the nano-scale range difficult and, therefore, only a part of the potential of the sol-gel process can be made use of so far.

In a further process monodisperse particles are prepared from aqueous salt solutions through controlled growth reactions in the solution phase. In this case the particle size and the particle shape are determined by various parameters. However, the formation of monodisperse particles necessitates a very exact adjustment of the reaction parameters and said particles can only be formed within a very narrow range. In order to avoid agglomerates in the solution, highly diluted solutions ( $10^{-4}$  to  $10^{-6}$  moles/l) are employed and, therefore, said processes are not very suitable for the production of powders.

In the hydrothermal synthesis oxides and hydroxides, respectively, are precipitated from corresponding inorganic salts at elevated temperatures and pressures in the presence of suitable precipitation agents. By suitably varying the reaction parameters, crystalline products having primary crystallite sizes down to a few nm may be obtained. Due to the presence of hard agglomerates which are formed during the synthesis, the processing of these powders is, however, difficult.

European patent application EP-A-363927 discloses a process for the preparation of suspensions containing spherical oxide particles (preferred size of from 1 to 2  $\mu\text{m}$ ) wherein an aqueous phase containing at least one element which can be precipitated in the form of an oxide(hydrate) in dissolved form or in the form of a sol is emulsified in an organic liquid. In said organic liquid at least one compound acting as phase transfer catalyst is dissolved. The emulsifiers employed according to EP-A-363927 generally have an HLB value of less than 7, in certain cases a value of more than 11 or higher.

Although even very fine powders have already been prepared by means of the emulsion technique there is to date no generally applicable and reliable process which makes it possible to generate particles having sizes of from 10 to 100 nm, particularly from 5 to 50 nm, by this route. Thus, the problem underlying the present invention was to provide a process for the preparation of suspensions containing oxide particles in the nano-scale range which, after a suitable removal of solvent, drying and optionally calcination, affords oxide powders having an average particle size of not more than 50 nm.

According to the present invention, said problem is solved by a process for the preparation of a suspension containing oxide particles in the nano-scale range wherein an aqueous phase containing at least one element capable of being precipitated as neutral, acidic or basic oxide(hydrate) in dissolved form is emulsified in an organic liquid to form a water-in-oil emulsion (W/O emulsion) and thereafter, by changing the pH value in the emulsified water droplets, the precipitation of the oxide(hydrate) in said droplets is caused, which process is characterized in that as emulsifier a

mixture of at least one non-ionic emulsifier having an HLB value of below 7 and at least one non-ionic emulsifier having an HLB value above 9 is used, the HLB value of the resulting mixture of emulsifiers ranging from 7.5 to 11.5, and that the volume ratio of the mixture of emulsifiers employed to aqueous phase is from 2.5:1 to 0.8:1.

In the following, the process according to the present invention will be explained in more detail.

The aqueous phase to be emulsified in the organic liquid contains, in dissolved form, at least one element capable of being precipitated in the form of an oxide(hydrate) by raising or lowering the pH-value.

According to the present invention, preferred elements are those which are suitable for the production of glass and ceramics, respectively. As examples of said elements there may be mentioned metals in general, particularly alkali metals (e.g. Li, Na, K), alkaline earth metals (e.g. Mg, Ca, Sr and Ba), other metals of the main groups such as, e.g. Al, Sn, Pb, Bi, metals of the subgroups such as, e.g., Ti, Zr, V, Mn, Nb, Ta, Cr, Mo, W, Fe, Co, Ni, Cu, Zn, and the lanthanides such as, e.g., Ce and Y.

Preferred examples of oxides to be precipitated are, i.a.,  $ZrO_2$ ,  $TiO_2$ , lead zirconate titanate (PZT),  $BaTiO_3$ ,  $Al_2O_3$ ,  $YBa_2Cu_3O_7$ ,  $Cr_2O_3$  and  $Fe_2O_3$ .

Preferably the above elements are present in the emulsified aqueous phase in form of their hydrolysable salts at salt concentrations of at least 20% and, particularly, at least 25% by weight. In view of an economically attractive yield the salt concentration should not be too low and particularly should not be less than 10% by weight, if possible, although it is apparent that in the case of compounds which are less readily soluble in water concentrations of 5% by weight and less are also acceptable. Saturated salt solutions may be employed (and if possible, should be employed).

Preferred among the salt solutions are those which (in the case of basic oxide(hydrates)) contain anions which are readily decomposable thermally, particularly nitrates, sulfates and anions of organic acids such as acetates and formates. However, other anions may be used as well, such as, e.g., halides, particularly chlorides and bromides. Tungstates, molybdates and silicates are examples of anions which cause precipitation in acidic media (pH <7).

Aqueous salt solutions may be prepared according to many processes familiar to those skilled in the art. In the simplest case the corresponding salt may simply be dissolved in water. Another option is, for example, the dialysis of salt solutions.

Apart from salt solutions aqueous sols may particularly be employed, too. Such sols may be prepared, e.g., by hydrolysing a metal alkoxide dissolved in a short-chain alcohol by addition of aqueous acid. Commercially available sols are, e.g.,  $\text{SiO}_2$  sols, water glass and Boehmit sols.

In order to form a water-in-oil emulsion the aqueous phase is emulsified in an organic liquid. According to the present invention the emulsification is carried out in the presence of a specific non-ionic emulsifier system which will be explained in more detail below.

Any organic solvent which is inert under the reaction conditions and substantially immiscible with water is suitable as organic liquid on principle. Examples thereof are (optionally halogenated, particularly fluorinated and/or chlorinated) aliphatic and aromatic hydrocarbons (e.g. hexane, heptane, decane, gasoline fractions, kerosene, mineral oil, benzene, toluene, xylene), higher alcohols (e.g. alcohols having 5 to 7 carbon atoms), ethers (such as tetrahydrofuran, dioxane, ethers derived from polyethylene glycol and polypropylene glycol), esters and ketones.

According to the present invention gasoline fractions (boiling range e.g. 50 to 70°C or 100 to 140°C), hexane, heptane, toluene, the xylenes and halogenated hydrocarbons such as, e.g., chloroform and chlorobenzene are preferably employed as organic liquid. The boiling point of the solvent should in any case be below the decomposition



temperature thereof. Since the organic solvent will later be removed preferably quantitatively it should not have too high a boiling point, particularly no boiling point which is substantially above 180°C. On the other hand, the boiling point should not be too low, i.e., not substantially less than 50°C, since otherwise the separation of the water which may later have to be carried out may become difficult.

The best solvent for a given system is dependent on many factors, but can be determined by the skilled person by means of simple routine experimentation.

According to the present invention, a mixture of at least two non-ionic emulsifiers is employed as emulsifier, at least one of said emulsifiers preferably having an HLB value below 5 and particularly below 3 while at least one other emulsifier preferably shows an HLB value above 10 and particularly above 11 (e.g. from 11 to 15).

Preferably a mixture of only two emulsifiers is used. In any case, the resulting emulsifier mixture has to have an HLB value ranging from 7.5 to 11.5, particularly from 8.5 to 10.5. Particularly preferred is an HLB value of 8.9 to 10.0. The relative amounts of emulsifiers thus result from the HLB values of the individual emulsifiers on the one hand and the desired HLB value of the mixture on the other hand.

The non-ionic emulsifiers employable according to the present invention are known to the skilled person. Specific examples of non-ionic emulsifiers which according to the present invention are particularly suitable are sorbitan esters of lauric, palmitic, stearic and maleic acids (e.g. those marketed under the trademark SPAN<sup>®</sup>), polyoxyethylene derivatives of said esters (e.g. those marketed under the trademark TWEEN<sup>®</sup>) and alkyl(phenol) polyglycol ethers and fatty acid polyglycol esters (e.g. those marketed under the the trademark EMULSOGEN<sup>®</sup>). As further examples emulsifiers of the ARLACEL<sup>®</sup>, PLURONIC<sup>®</sup>, EMULAN<sup>®</sup>, MALOPHEN<sup>®</sup> and MALOVET<sup>®</sup> types may be mentioned. Of course, the just mentioned emulsifiers only

represent a small selection of emulsifiers employable according to the present invention.

In the selection thereof one should preferably choose emulsifiers which are structurally as similar as possible. For example, this is the case with the pair Tween<sup>®</sup> 80/Emulsogen<sup>®</sup> OG. Tween<sup>®</sup> 80 (HLB value = 15) is a polyoxyethylene (20) sorbitan monooleate while Emulsogen<sup>®</sup> OG (HLB value = 3) also is an ester of oleic acid (polyglycerol ester of oleic acid).

Furthermore, it is advantageous to have also an as close structural resemblance as possible between dispersion medium (oil phase) and emulsifier system. For example, petrol ether is much more suitable for the above pair of emulsifiers than e.g. xylene.

The emulsifier mixture employed according to the present invention is employed in a volume ratio with respect to the aqueous phase of 2.5:1 to 0.8:1, preferably 2.1 to 1:0.9 and particularly 1.5:1 to 1:1.

The emulsifier employed according to the present invention i.a. acts as protective colloid and thus can prevent the agglomeration of particles in the nano-scale range. This may also be beneficial in the calcination of said fine particles since the present emulsifiers decompose completely only at temperatures  $\geq 400^{\circ}\text{C}$  and at said temperatures the deactivation of the particle surface by elimination of  $\text{H}_2\text{O}$  has already proceeded to a substantial extent which prevents or minimizes, respectively, a growing together of the particles.

Particularly if the preparation of monodisperse powders is desired, it may be advantageous to employ an auxiliary agent in addition to the emulsifier mixture used according to the present invention, said auxiliary agent being preferably selected from higher alcohols, particularly those having 8 to 15 carbon atoms such as, e.g. octanol, decanol, dodecanol and tetradecanol. Preferably, such an auxiliary agent is employed in amounts of from 0.1 to 15%, particularly 0.5 to 10% and particularly preferred from 1 to 5% by volume, based on the emulsion.

The use of an auxiliary agent (e.g. octanol) is beneficial in various respects and therefore is preferred according to the present invention (particularly at higher W/O ratios). Particularly, the use of such an auxiliary agent makes it possible to substantially reduce the amount of emulsifier to be employed without having to accept that thereby simultaneously the emulsified water droplets become larger. This is advantageous from an economic point of view since thereby either with the droplet size being the same emulsifier can be saved (resulting in less environmental pollution) or the droplet size may be reduced at a constant amount of emulsifier (which otherwise is only possible by decreasing the volume ratio aqueous phase/oil phase which is undesirable from an economic point of view).

By adding an auxiliary agent, the salt concentration in said water droplets may be increased without jeopardizing the stability of the emulsion, allowing an increase of the yield of powder.

Finally, an otherwise bimodal particle size distribution may in many cases be converted into a monomodal distribution by the use of an auxiliary agent.

With respect to the volume ratio auxiliary agent/emulsifier system it is to be noted that values  $>1:1$  usually do not result in stable emulsions. An optimum ratio generally ranges from  $0.05:1$  to  $0.5:1$ , particularly from  $0.07:1$  to  $0.3:1$ .

Particularly at higher W/O ratios too high an emulsifier concentration may, moreover, result in an (undesired) bimodal particle size distribution.

According to the present invention, the volume ratio aqueous phase/oil phase (organic liquid) preferably is  $0.1:1$  to  $0.5:1$  and particularly  $0.15:1$  to  $0.3:1$ . While there is no practical minimum value for the volume ratio of the aqueous phase, the upper limit of said volume ratio of the aqueous phase is determined by the point of inversion (i.e. the conversion from a W/O emulsion into an O/W emulsion). The point of inversion is specific for each system and may readily be determined (e.g. by determining the change in

conductivity). Generally it may, however, be stated that with increasing proportion of water the stabilization of extremely small droplets becomes increasingly difficult. Moreover, a strong increase in the viscosity may cause problems in the precipitation, particularly if phase transfer catalysts are employed (see below), since the rate of exchange thereof decreases sharply with increasing viscosity. Emulsions having an as low viscosity as possible are thus desirable and for that purpose the volume ratio of the aqueous phase of the emulsion should not exceed 30%. Furthermore, the range or existence of a stable (micro)emulsion is dependent both on the ratio aqueous phase/oil phase and on the ratio emulsifier mixture/aqueous phase (and on the addition of an auxiliary agent).

Techniques known to the skilled person may be used for the preparation of the emulsion. For example, the emulsifier system may first be dissolved in the organic liquid and then the aqueous phase may be added thereto in one portion or gradually, e.g., with stirring. The preparation of the emulsion is preferably effected at room temperature or slightly elevated temperatures (e.g. 40 to 50°C). Ultrasonic devices or rotor-stator systems of high shear rate, but also magnetic stirrers (for droplet sizes around 500 nm and below) may, for example, be used. The size of the formed oxide particles is determined particularly by the droplet size of the emulsion and the solids content of the aqueous solution. The bigger the emulsified water droplets, the bigger the oxide particles in the suspension will become. Preferably, the upper limit for the droplet size in the emulsion is 500 nm. The preferred lower limit for the droplet size depends on the desired size of the oxide particles. However, it has to be taken into account that the particle size after removal of the water may be substantially smaller than the original droplet size.

For forming the W/O-emulsion one may, for example, also convert a O/W emulsion into a W/O emulsion by adding organic liquid.

The change (raising and lowering, respectively) of the pH value in the emulsified water droplets in order to precipitate the neutral, acidic or basic oxide(hydrates) required in the process of the present invention may on principle be effected by adding any basic or acidic, respectively, compound which is soluble in the aqueous

phase to a sufficient extent. In the process according to the present invention the increase of the pH value is preferably accomplished by adding (optionally gaseous) ammonia and/or organic bases (e.g. amines such as dimethylamine, triethylamine, etc.). Said compounds show the advantage of later being removable by a corresponding thermal treatment of the oxide particles without leaving any residues. For lowering the pH value inorganic or organic acids such as, e.g., HCl and acetic acid may, for example, be employed. This applies particularly to oxide systems which include no anions such as, e.g.,  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{SiO}_2/\text{TiO}_2$ ,  $\text{GeO}_2/\text{TiO}_2$  etc.

According to a particularly preferred embodiment of the present invention a compound acting as phase transfer catalyst is added to the organic phase in order to raise or lower the pH value, said compound being capable of replacing the anions and cations (e.g.  $\text{NH}_4^+$ ), respectively, contained in the emulsified water droplets by hydroxide ions and protons, respectively, thereby effecting the precipitation of the oxide(hydrates) in said droplets.

Said compound acting as phase transfer catalyst may be a quaternary ammonium, phosphonium or other onium compound in the case of raising the pH value. Crown ethers and cryptands are, among others, also suitable according to the present invention.

Due to their ready availability and their price ammonium compounds are preferred. Particularly preferred examples are the quaternary ammonium salts, particularly tetraalkylammonium chlorides, bromides and iodides. In said tetraalkylammonium salts the alkyl radicals, which may be the same or different, preferably have 1 to 20 carbon atoms. The total number of carbon atoms should be high enough so that said salts are substantially insoluble in water and thus is preferably above 15, particularly above 20. Tetraalkylammonium salts having 2 to 3 long radicals (e.g. having 8 to 20 carbon atoms) and one or two short alkyl groups (e.g. one or two methyl or ethyl groups) have proved to be particularly suitable representatives. One example thereof is didodecyldimethylammonium bromide. A further preferred class of tetraalkylammonium salts are those which have one long hydrocarbon radical (e.g. having 16 or more carbon atoms) and three short alkyl groups (e.g. methyl or ethyl groups). An example

thereof is octadecyl trimethyl ammonium bromide. Generally it can be stated that tetraalkyl ammonium salts having radicals different from each other are more advantageous than those having four identical radicals. Said alkyl radicals may also be substituted, e.g., by a phenyl group. When selecting the tetraalkylammonium salt one also has to take into account that salts having long alkyl chains may act as surfactants. Accordingly one has to determine by simple routine experimentation for each particular case which phase transfer catalyst is most suitable.

Suitable phase transfer catalysts for an intended lowering of the pH value are, e.g., carboxylic acids having medium chain lengths (e.g.  $C_8$ - $C_{16}$ ) which as such and particularly in the form of a salt show a sufficient solubility in the organic medium (e.g. stearic acid, lauric acid and oleic acid).

The compound acting as phase transfer catalyst may be dissolved in the organic liquid or also in the final emulsion. The dissolution may be effected at room temperature or slightly elevated temperature, preferably with stirring. If it is possible to dissolve the compound acting as phase transfer catalyst in the organic phase already prior to the emulsification operation, the advantage thereof is that the reuse of the organic phase is simplified.

In order to facilitate the dissolution of the phase transfer catalyst in the organic liquid or in the organic phase of the emulsion it is preferred to dissolve said phase transfer catalyst in an as small as possible volume of a good solvent, particularly an alcohol having 4 to 8 carbon atoms, preferably hexanol, heptanol or octanol, prior to its addition to the system. The solvent for the phase transfer catalyst should be substantially insoluble in water in order to assure a distinct phase separation in the emulsion and is preferably identical with the auxiliary agent described above.

The compound acting as phase transfer catalyst, e.g., the tetraalkylammonium salt may already be used in the hydroxide form and also in stoichiometric amounts relative to the anions to be exchanged and present in the aqueous phase. Preferably, however, the compound acting as phase transfer catalyst is used in sub-

stoichiometric amounts, particularly 1 to 20%, preferably 5 to 10%, based on the anions to be exchanged and present in the aqueous phase. In this case the phase transfer catalysts should, of course, be regenerated in a batchwise or continuous manner. According to a particularly preferred embodiment of the present invention, exchange of the anions and regeneration of the phase transfer catalyst take place simultaneously. The presence of the phase transfer catalyst in the hydroxide form already at the beginning affords the additional advantage that the first exchange occurs spontaneously and hydroxides are formed immediately on the surface of the water droplets, resulting in a substantial stabilization of the emulsion so that said mode of operation is particularly recommendable with less stable emulsions.

As regenerating agents for the compound acting as phase transfer catalyst (anionic and cationic, respectively) ion exchange resins are preferably employed.

Ion exchange resins suitable according to the present invention are those which are conventional and commercially available. Inorganic ion exchangers may be used, too.

The regeneration of the compound acting as phase transfer catalyst may be carried out in different ways. For example, the emulsion may be passed through the ion exchange column together with the phase transfer catalyst, the residence time of the emulsion on the column being adjusted so that the exchange and regeneration of the phase transfer catalyst are complete. For that purpose it is also possible to pass the emulsion through the column several times. As already mentioned above, it is also possible to use the phase transfer catalyst in stoichiometric amounts, separate it after the exchange has taken place and to regenerate and reuse it.

Following the (complete) precipitation of the desired oxide (hydrates) the initially employed emulsion is present in the form of a suspension of oxide(hydrate) particles in the nano-scale range. The water is preferably separated from said suspension in order to densify and stabilize the particles. To that end the water is distilled off, e.g., azeotropically (preferably at atmospheric

pressure). Minor amounts of hydroxides dissolved in the aqueous phase precipitate by said water removal. Azeotropic mixtures containing 20 to 40% of water may be achieved by e.g. addition of a little (e.g. 10% by volume of the aqueous phase) butanol and/or pentanol, i.e., alcohols which are still miscible with  $H_2O$  to a certain extent, to mixtures of water and petrol ether. The separation of the water from the distillate may be effected by means of a Dean-Stark water trap. Preferably the organic phase is also distilled off and then optionally recycled.

The oxide particles thus prepared may then be dried. The powders obtained may be further processed in usual manner, e.g., by calcining them and optionally subsequently converting them into molded bodies by pressing and sintering. The powder suspension obtained may, however, be also further processed, directly or following the removal of water, by feeding it e.g. to a filter press and processing it therein into molded bodies.

The following example illustrates the process according to the present invention without limiting it.

#### EXAMPLE 1

To 50 ml of petrol ether (boiling range 50 to 70°C) 5 ml each of EMULSOGEN<sup>®</sup>OG and TWEEN<sup>®</sup>80 were added. Following the complete dissolution of the emulsifiers 10 ml of water in which 10% by weight of  $Cr(NO_3)_3$  or  $FeCl_3$  or  $Al(NO_3)_3$  were dissolved were added dropwise. Thereafter, 3 ml of n-octanol were added. The sonification of the resulting two-phase system resulted in a clear translucent emulsion. The precipitation of the corresponding hydroxides and oxides, respectively, was effected by passing gaseous  $NH_3$  through the emulsion. Due to the precipitation of the oxides and hydroxides, respectively, the emulsions turned into the typical colours of said compounds but did not change in transparency. The water was removed by azeotropic distillation and subsequently the petrol ether was also distilled off. There was obtained a translucent mass in which the powder particles were dispersed. By calcination between 200 and 400°C (e.g. 5 hours at 350°C) a powder was obtained therefrom.



In the above emulsions the initial droplet size was about 260 nm and decreased only a little to 200 nm after the reaction with ammonia. In the case of the chromium salt the particle size after the azeotropic removal of water was, however, only about 20 nm. In the case of  $\text{Al}(\text{NO}_3)_3$  Boehmit having a uniform particle size of 20 nm was obtained after the calcination of the residue (8 hours at  $350^\circ\text{C}$ ) and in the case of  $\text{FeCl}_3$  the particle size of the  $\text{Fe}_2\text{O}_3$  powder after 5 hours at  $350^\circ\text{C}$  also was uniformly 20 nm.

Thus, it is apparent that the precipitates inside the droplets are packed very loosely and may be densified by simple azeotropic distillation. For the preparation of powders in the nano-scale range it is thus not necessary for the droplet size of the initial emulsion to be already as small as the desired particle size.

#### EXAMPLE 2

In example 1 e.g. a 10% by weight aqueous solution of e.g.  $\text{Cr}(\text{NO}_3)_3$  was used as aqueous phase. Since said chromium salt shows a very high solubility in water, the oxide may be prepared in high yield via the corresponding emulsified salt solution. Only very diluted solutions can, however, be prepared from salts which are scarcely soluble in water and, consequently, the oxide powders may only be synthesized in low yields from the corresponding emulsions. In order to be able to also prepare such oxide powders in high yields, a different route for the preparation of the aqueous phase has to be taken, therefore, e.g., via the preparation of a sol.

A solution of 70% by weight of  $\text{Zr}(\text{O}-n\text{-C}_3\text{H}_7)_4$  in n-propanol (55 g) was dissolved in 400 ml of ethanol and a mixture of 11 ml  $\text{HNO}_3$  (65% by weight) and 12.5 ml water was dropwise added thereto. Thereafter the solvent was removed at  $50^\circ\text{C}$  and 20 kPa. Following the addition of 249 ml of  $\text{H}_2\text{O}$  a sol which contained 10% by weight of Zr salt formed. Said sol was emulsified in petrol ether, the volume ratio sol:petrol ether being 0.2:1. The organic phase showed a volume ratio petrol ether/emulsifier (as in example 1)/n-octanol of 10:1:0.6.

By passing gaseous ammonia into the emulsion a solid was formed whereafter the water was azeotropically distilled off and the

suspension thereby was densified following the addition of 10% by volume of n-butanol (based on the aqueous phase). After evaporation of the solvent and calcination of the residue (5 hours at 350°C) a  $\text{ZrO}_2$  powder was obtained. When densifying said precipitate, the particle size decreased from 240 nm to 10 nm. The calcined powder also showed a (very uniform) particle size of about 10 nm. The individual particles were still agglomerated to a very small extent, which is due to the surface passivating action of the emulsifier system.

### EXAMPLE 3

By means of the process described in the following also multiple component systems (e.g.  $\text{Y}_2\text{O}_3$ -stabilized  $\text{ZrO}_2$ ) may be prepared. A Zr sol (compare example 2) wherein  $\text{Y}(\text{NO}_3)_3$  was dissolved (3 - 8% by moles based on Zr) served as aqueous phase.

A solution of 70% by weight of  $\text{Zr}(\text{O}-n\text{-C}_3\text{H}_7)_4$  in n-propanol (11 g) was dissolved in 80 ml of ethanol and a mixture of 2.2 ml of  $\text{HNO}_3$  (65% by weight) and 2.5 ml of  $\text{H}_2$  was added dropwise thereto. Subsequently the solvent was removed at 50°C and 20 kPa. Following the addition of 23.76 ml of water in which 0.4 g of  $\text{Y}(\text{NO}_3)_3$  were dissolved, a sol which contained 20% by weight of salt was formed. The  $\text{Y}_2\text{O}_3$  content of said Zr sol was 3% by moles. Said sol was emulsified in petrol ether, the volume ratio sol : petrol ether being 0.2:1. The organic phase showed a volume ratio petrol ether/emulsifier (as in example 1)/n-octanol of 5:1:0.17.

The solid was formed by passing gaseous ammonia into the emulsion. Following the addition of 10% by volume of n-butanol (based on the aqueous phase) the water was removed by azeotropic distillation and the suspension was densified. After the removal of the solvent the residue was calcined (5 hours at 380°C). The powder obtained,  $\text{Y}_2\text{O}_3$ -stabilized  $\text{ZrO}_2$  (tetragonal), had a particle size between 3 and 5 nm. The individual particles were still agglomerated to a very small extent, which is due to the surface passivating action of the emulsifier.

CLAIMS:

1. Process for the preparation of a suspension containing oxide particles in the nano-scale range, wherein an aqueous phase containing at least one element capable of being precipitated as neutral, acidic or basic oxide(hydrate) in dissolved form is emulsified in an organic liquid to form a water-in-oil emulsion and thereafter, by changing the pH value in the emulsified water droplets, the precipitation of the oxide(hydrate) in said droplets is caused, characterized in that as emulsifier a mixture of at least one non-ionic emulsifier having an HLB value of below 7 and at least one non-ionic emulsifier having an HLB value above 9 is used, the HLB value of the resulting mixture of emulsifiers ranging from 7.5 to 11.5, and that the volume ratio of the mixture of emulsifiers employed to aqueous phase is from 2.5:1 to 0.8:1.

2. Process according to claim 1, characterized in that at least one emulsifier having an HLB value below 5, and particularly below 3, is used.

3. Process according to any one of claims 1 and 2, characterized in that at least one emulsifier having an HLB value above 10, particularly above 11, is used.

4. Process according to any one of claims 1 to 3, characterized in that the HLB value of the resulting emulsifier mixture ranges from 8.5 to 10.5, and particularly from 8.9 to 10.

5. Process according to any one of claims 1 to 4, characterized in that the volume ratio of emulsifier mixture to aqueous phase is from 2:1 to 1:0.9, and particularly from 1.5:1 to 1:1.

6. Process according to any one of claims 1 to 5, characterized in that the aqueous phase/oil phase volume ratio

in the emulsion is from 0.1:1 to 0.5:1, and particularly from 0.15:1 to 0.3:1.

5 7. Process according to any one of claims 1 to 6, characterized in that a salt solution is used as aqueous phase and the salt concentration in the water droplets is preferably at least 20 wt.-%.

10 8. Process according to any one of claims 1 to 7, characterized in that in addition to the emulsifier mixture at least one aliphatic alcohol having 8 to 15 carbon atoms is employed, preferably in amounts of 0.1 to 15% by volume, based on the emulsion, and at a volume ratio with respect to emulsifier mixture of at least 1:1.

15 9. Process according to any one of claims 1 to 8, characterized in that the element to be precipitated as oxide(hydrate) is at least one of the group of alkaline earth metals, particularly barium, lanthanides, particularly yttrium, the metals of the sub-groups, particularly titanium, zirconium, niobium, tantalum and tungsten, and/or is aluminum, tin, lead.

20 10. Process according to any one of claims 1 to 9, characterized in that an optionally halogenated aliphatic or aromatic hydrocarbon or a mixture thereof is employed as organic liquid.

25 11. Process according to any one of claims 1 to 10, characterized in that (at least) one basic or neutral oxide(hydrate) is precipitated and the pH value in said droplets is raised.

30 12. Process according to claim 11, characterized in that the raising of the pH value is effected by adding ammonia and/or an organic amine or by means of a phase transfer catalyst.

13. Process according to claim 12, characterized in that said phase transfer catalyst is an ammonium salt, particularly a tetra(ar)alkylammonium halide.

5           14. Process for the preparation of oxide particles in the nano-scale range, characterized in that the water and the organic liquid are removed from a suspension prepared according to the process of any one of claims 1 to 13, preferably  
10 by (azeotropic) distillation, the particles obtained are dried and optionally calcined.